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Antimicrobial Coatings Obtained in an Atmospheric Pressure Dielectric Barrier Glow Discharge

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ABSTRACT

This paper addresses the development of plasma polymer coatings that should prevent bacteria from adhering to medical devices, implants, textile fibers, packaging materials, etc. The two main parameters affecting bacterial colonization onto surfaces are the surface energy and the surface roughness. Both parameters can be adjusted by the deposition of a thin plasma polymer coating in an atmospheric pressure dielectric barrier glow discharge. According to SEM, FTIR, SPM, XPS and contact angle measurements, smooth, hydrophilic plasma polymer coatings were obtained under specific plasma conditions starting from 2-hydroxyethyl methacrylate (HEMA) and ethyl diazoacetate (EDA).

INTRODUCTION

In the initial step of bacterial cell adhesion, proteins are adsorbed onto a surface [1]. Moreover, some bacteria strains produce a polysaccharide based matrix referred to as slime, which provides them with an additional mechanism for adhesion and an increased resistance to antibiotic drug therapies [2]. The reduction of protein and polysaccharide adsorption onto surfaces is therefore an important issue in the development of improved materials for medical applications such as implants, prostheses, shunts, intraocular or contact lenses and medical devices. Besides, this is also a topic in the development of food grade or medical grade plastic foil and textile fiber.

Despite the lack of a theory on the role of hydrophobicity on protein adhesion, it is reported in the literature that surfaces of low surface energy adsorb more proteins than surfaces of high surface energy [3-6]. Moreover, proteins show better adhesion to rough surfaces [7, 8].

Common low-pressure nonequilibrium plasmas represent an excellent method to deposit a very thin polymeric film (typically 2-100 nm) with mentioned desirable surface properties [9, 10]. The application of low-pressure plasmas is however limited due to the need of vacuum equipment and the low deposition rates that can be obtained.

Therefore, both the industrial and the academic world show a growing interest in plasma processes at atmospheric pressure. So far, applications were mainly situated in the area of cleaning, sterilization and activation of plastic surfaces, but currently the focus is shifting towards the deposition of organic and inorganic functional coatings on various substrates [11]. Like the low-pressure plasma techniques, atmospheric pressure dielectric barrier glow discharges allow treatment of a variety of objects, foils, fibers, etc in a sterile environment and at room temperature. In addition, the atmospheric pressure set-up allows continuous processing, which is especially interesting for the treatment of textile and plastic foil, while it allows significantly

higher deposition rates. More information on the theoretical background of this process can be found elsewhere [12-14].

EXPERIMENTAL SETUP

The experimental setup (see figure 1) of the dielectric barrier glow discharge (DBD) consists of two parallel electrodes (160x180 mm), both covered with an insulating Al_2O_3 plate of 2 mm thickness. To ensure stable plasma operation, the gap between the electrodes is limited to a few millimeters. Standard purity nitrogen and argon were used as inert carrier gases. The flow rate was controlled by mass flow controllers and set at 15 l/min. The reactive precursor is added to the inert carrier gas by means of an atomizer which generates a polydisperse submicron aerosol. In order to perform tests in a controlled environment, the electrode configuration is mounted in a closed chamber which is evacuated and subsequently filled with the carrier gas before deposition is started.

Plasma discharges were generated by a 20 kV/200 mA AC power supply with variable frequency, in this case ranging between 1 and 4 kHz.

The precursor molecules chosen in order to obtain coatings with high surface energies, are 2-hydroxyethyl methacrylate (HEMA, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COO}_2\text{CH}_2\text{CH}_2\text{OH}$) and ethyl diazoacetate (EDA, $\text{N}_2\text{Cl}(\text{CO}_2\text{C}_2\text{H}_5)_2$) (Sigma-Aldrich, Belgium), both containing a polar functional group. Each of the precursors was polymerized in N_2 and Ar plasma in runs of 2 and 6 minutes.

Double polished silicon substrates (12 x 12 mm) were used as substrates for plasma polymer deposition and placed on the lower (high voltage) electrode. The coatings obtained were analyzed by FESEM (JSM-6340F, JEOL, USA), SPM (Digital Instruments, USA), XPS (Fisons Instruments, USA) and FTIR-spectroscopy (Avatar 360 ESP, Nicolet, USA). Contact angles were measured using the sessile drop technique (SOCA 15 plus, Dataphysics Instruments GmbH, Germany).

DISCUSSION

A first observation is that the carrier gas (N_2 or Ar) has a strong influence on the polymerization process [11]. So far, it appeared however difficult to establish a correlation between the carrier gas and the details of the polymerization process. In spite of this fact, some qualitative observations could be readily made.

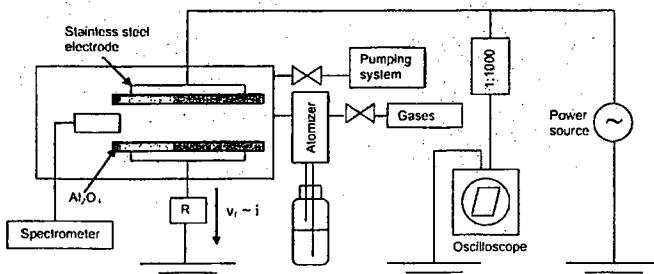


Figure 1. Experimental set-up of atmospheric pressure dielectric barrier glow discharge.

Microscopy

Figure 2 shows the SEM cross-sections of the coatings resulting from the deposition of HEMA on silicon obtained in a N₂ and Ar plasma. After a deposition time of 6 minutes, both coatings showed a similar structure although the 'polymer' structure obtained in N₂ appears slightly more dense. Together with the difference in deposition rate this gives an indication of differences in the polymerization mechanism. The coatings prepared starting from EDA resemble the ones presented in figure 2 although thicknesses of about 400 and 550 nm were obtained in N₂ and Ar, respectively. The coating thicknesses obtained after 2 minutes demonstrated constant deposition rates as a function of time.

An important feature in the present context is the roughness of the coatings, which proved to be very low according to SPM measurements. Surface roughnesses between 0.20 and 0.35 nm were obtained in both Ar and N₂ plasma.

Contact Angles

Contact angles of the plasma polymer coatings were determined and summarized in table 1. Under equal reaction conditions, HEMA based plasma polymers were characterized by lower contact angles than those prepared from EDA. In addition, it should be noted that the contact angles of the EDA plasma polymers remain constant, while those of the HEMA based coatings decrease somewhat after the first contact of the droplet with the surface. This could be due to the absorption of water in the coating. It is however striking that the carrier gas has more impact on the contact angle of the plasma polymers than the nature of the precursor. In N₂ plasma, both HEMA and EDA give rise to the deposition of coatings with contact angles lower than 20°, whereas the contact angles obtained in Ar plasma are significantly higher. XPS and FTIR analysis were necessary to gain a better insight in the present phenomena.

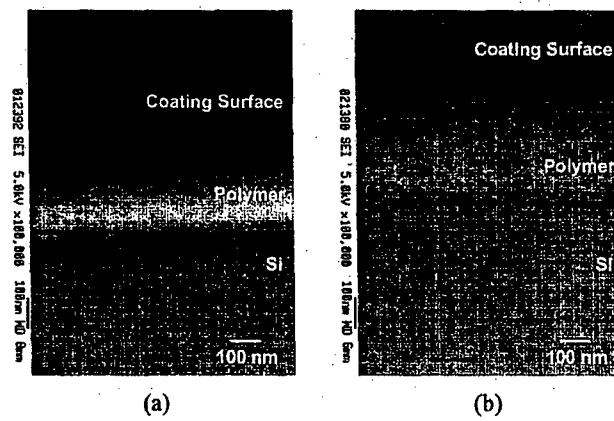


Figure 2. SEM cross sections of plasma polymer coatings obtained from HEMA in N₂ (a) and Ar plasma (b) after 6 minutes.

Table 1. Contact angles with water ($\theta_{\text{H}_2\text{O}}$) of plasma polymer coatings obtained from HEMA and EDA in N₂ and Ar DBD glow discharges (deposition time of 6 minutes).

Precursor/Carrier Gas	$\theta_{\text{H}_2\text{O}}$ (deg)
EDA / N ₂	19.2
EDA / Ar	46.7
HEMA / N ₂	16.1
HEMA / Ar	34.2

XPS

X-ray photoelectron analysis was used to determine the relative amounts of C, O and N at the polymer film surfaces (Table 2). Apparently, more nitrogen is incorporated at the surface of plasma polymer coatings when N₂ is used as carrier gas instead of Ar. This is manifestly demonstrated by the polymerization of HEMA, which resulted in a surface concentration of nitrogen of about 30 % in N₂ plasma and 0 % when the deposition was carried out in Ar plasma. The latter can be rationalized by the incorporation of N-containing radicals present in a N₂ plasma into the bulk of the plasma polymers and thus at their surface. On the other hand, stable radicals of organic origin that remain present in plasma polymer coatings after polymerization might react with N₂ even in the absence of plasma conditions, e.g. during storage. Providing this interpretation is legitimate, only the upper layers of the coatings will contain the observed amounts of N. More evidence for one of these explanations may arise from FTIR measurements.

The observations made for HEMA concerning the C/N ratio of the plasma polymers also hold for the case of EDA. However, while EDA itself is characterized by a C/N ratio of 2, this ratio increased after polymerization in N₂ and Ar to 6.5 and 18.1, respectively. Clearly, the diazo-group of EDA has a tendency to split off under plasma conditions. The nitrogen containing functionalities at the surface of the EDA coatings are therefore not necessarily of diazo-origin.

When comparing the contact angles of the coatings with their surface composition, it is however obvious that the high N-content should be responsible for the low contact angles obtained after polymerization in N₂ plasma.

Table 2. XPS-data (surface mole fraction of elements excluding hydrogen in %) obtained from HEMA and EDA plasma polymer coatings prepared in N₂ and Ar DBD glow discharges.

Precursor/Carrier Gas	C _{tot}	O _{tot}	N _{tot}
EDA / N ₂	65.9	24.1	10.0
EDA / Ar	63.4	33.1	3.5
HEMA / N ₂	54.8	14.7	30.5
HEMA / Ar	69.8	30.2	0.0

FTIR

Infrared spectra of the plasma polymers on silicon are presented in figure 3. As expected from the previous sections, the nature of the carrier gas causes some substantial differences in the FTIR spectra.

The spectrum of the HEMA based coating obtained in Ar plasma (fig. 3.a) contains the main bands typical for the monomer, including O-H stretching (3422 cm^{-1}), C-H stretching (2955 cm^{-1}), C=O stretching (1730 cm^{-1}) and C-H deformation (1456 cm^{-1}). In the spectrum obtained from the HEMA based plasma polymer deposited in N_2 , the weak band at 3317 cm^{-1} could be attributed to O-H stretching. However, the N-H bond in amines and amides may also cause absorption in the region of $3500\text{-}3300\text{ cm}^{-1}$. Thus, although the low intensity of the absorption bands complicates the identification of the different functionalities, it seems reasonable to assume that amine and/or amide groups are incorporated in the HEMA based plasma polymer when N_2 is used as a carrier gas.

The most striking feature in the spectra of the plasma polymers obtained from EDA (fig. 3.b) is the absence of the absorption band typical for the diazo-group at $2200\text{-}2000\text{ cm}^{-1}$, which confirms that this group is split off from the precursor when introduced into plasma. As a result, only C-H deformation (1447 cm^{-1}) and C-H (2982 cm^{-1}) and C=O (1737 cm^{-1}) stretching bands are identified in the spectrum of EDA based polymers deposited in Ar plasma. The same absorption bands are present in the spectrum of the EDA coatings that were polymerized in N_2 . The peaks originating from C-H stretching (2982 cm^{-1}) are however largely covered by two bands which are typical for the N-H stretching in $-\text{NH}_2$ (3146 and 3049 cm^{-1}).

In spite of their absence in these spectra, the presence of certain other functional groups at the surface of the coatings cannot be excluded as the intensity of their absorbance pattern could be too low to allow detection using common FTIR. It can however be stated that amine or possibly also amide groups are at least partly responsible for the high surface energies obtained when HEMA and EDA are polymerized in N_2 plasma. Ester groups, and in the case of HEMA also hydroxyl groups, are present in the coatings polymerized in both Ar and N_2 .

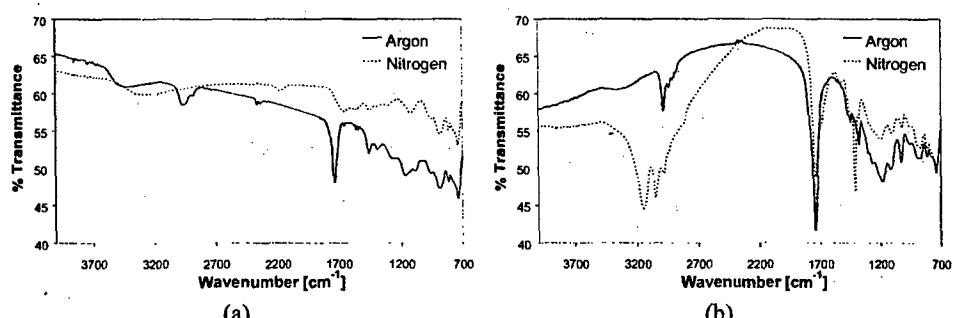


Figure 3. Infrared spectra obtained from HEMA (a) and EDA (b) in argon and nitrogen plasma.

CONCLUSIONS

This study shows that organic coatings with low contact angles and a low surface roughness can be obtained through polymerization of HEMA and EDA in a dielectric barrier glow discharge at atmospheric pressure. Especially when N₂ is used as a carrier gas, contact angles lower than 20° could be obtained mainly due to the incorporation of nitrogen in the plasma polymers. The true potential of these plasma polymers as antimicrobial coatings seems therefore promising but is currently being investigated in more detail.

As the present technique allows continuous processing at low temperature and at atmospheric pressure, it is in particular interesting for the treatment of large surfaces and plastic foils or fibers.

In addition, this technique offers promising perspectives for the further development of antimicrobial coatings in that intrinsically antimicrobial substances can be mixed with the precursor and thus incorporated in plasma polymer coatings.

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